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TITLE: Modification of subsurface region of polymers and carbon-based materials

Brief Summary Text (11):

Kapton and epoxies have LEO erosion yields of about  $(2.5-3) \times 10^{-24}$  cm<sup>3</sup>/at, which translates to  $(3-4) \times 10^{-24}$  g/atom of atomic oxygen. Many other polymers and carbon-based materials, such as graphite, carbon fiber-carbon composites and CFRP composites also have erosion rates of this order of magnitude, typically about  $(1-4) \times 10^{-24}$  g/atom. Perfluorinated polymers are an exception, because of the fluorine in their bonding structure, their erosion yields are much lower. Although it was once thought that perfluorinated polymers were an answer to the problems of polymers in LEO, there is a synergistic effect between atomic oxygen and VUV radiation that increases the erosion yield to unacceptable levels. Materials having erosion yields on the order of  $10^{-24}$  g/atom are unsuitable for long term use in the LEO environment, and space in general.

Brief Summary Text (15):

An example of such a thin film coating is disclosed in U.S. Pat. No. 5,424,131 (Wertheimer et al.). Wertheimer teaches the deposition of a thin barrier film, preferably via a plasma, on the surface of an organic polymer such as Kapton, Mylar or epoxy resin. The materials comprising the films are plasma polymers, inorganic insulating films, and semiconducting and conductive materials. As shown in the examples of Wertheimer, all of these materials preferably contain silicon. After the polymers were coated, they were exposed to oxygen atoms in a simulated LEO environment. Although not disclosed by Wertheimer, this exposure to oxygen atoms would convert the silicon-containing coating on the polymer surface into a coating of silicon dioxide.

Brief Summary Text (16):

In one example of Wertheimer, Kapton is coated with a thin film of the plasma polymer hexamethyldisiloxane and subsequently exposed to AO. A skin of SiO<sub>2</sub> forms on top of the plasma polymerized HMDSO coating during the initial stages of AO exposure, thereby protecting it from further attack and fulfilling the protection from the AO exposure. However, the cyclic mode of degradation of siloxane protective coatings in an oxygen environment implies an induction period prior to the onset of measurable degradation. This may be the reason why the siloxane materials flown in short duration space shuttle flights have appeared to be stable over the time period during which they were exposed. For extended space flights, however, these coating materials have a finite lifetime determined by their thickness and the AO flux. This problem is widely recognized in the space community.

Brief Summary Text (19):

It is known that selective silylation processes are used with positive polymer-based photoresists in the manufacture of semiconductor devices. The SiO<sub>2</sub> type enriched layer of these photoresists is typically formed by silylation of active groups in exposed areas of the photoresist followed by plasma development of the resist by reactive oxygen plasma etching. The SiO<sub>2</sub> type enriched layer is typically formed during the first few moments of etching. Silylated areas of the surface are etched at a lower rate than unsilylated areas, resulting in an etched pattern in the surface of the photoresist.

Drawing Description Text (4):

FIG. 2 is a graph of water contact angle versus time for the activation of Kapton;

Drawing Description Text (8):

FIG. 6 is a reaction sequence showing the wet process for activation of Kapton; and

Detailed Description Text (8):

Preferably, metallized polymer films comprise an aluminized film of polyimide, most preferably Kapton. Preferred composite materials include those containing carbon/graphite fibers in a polymeric resin or carbon matrix. The carbon/graphite fibers that reinforce the above composites can also be protected by this technique. Although, strictly speaking, these fibers are not polymeric materials, they are typically derived from polymeric materials such as polyacrylonitrile, and for convenience are sometimes referred to throughout this application as polymers or polymeric materials.

Detailed Description Text (9):

For space applications, the most preferred polymers which may be modified according to the present invention include polyimides, such as PMDA-ODA polyimide sold under the trade mark Kapton by Du Pont and having the repeating unit shown below, and aluminized Kapton; poly (ether ether ketone) such as that known as PEEK having the repeating unit shown below, and advanced composite materials, such as those comprising carbon fibers bonded with resin such as epoxy resins, carbon fibers in a PEEK matrix, and carbon fibers produced from poly(acrylonitrile) (PAN) precursor material. ##STR1##

Detailed Description Text (17):

UV radiation comprises radiation in the region of the electromagnetic spectrum including wavelengths from about 100 to about 380 nm. The preferred wavelengths to which substrates are exposed in the activation step is variable, and depends on the composition of the specific substrate. For example, polyimides such as Kapton are preferably irradiated with UV radiation having wavelengths from about 200 to about 300 nm. Kapton itself is preferably irradiated at wavelengths of 185 and 254 nm, primarily 254 nm.

Detailed Description Text (18):

Preferably, the source of UV radiation is a low-pressure quartz-mercury lamp having an intensity of from about 1 to about 5 mW/cm.<sup>sup.2</sup>. Taking Kapton as an example, a particularly preferred intensity is about 2.8 mW/cm.<sup>sup.2</sup>. Preferably, the molecular oxygen may be supplied as pure oxygen, oxygen combined with other gases, or air, with air being preferred for simplicity.

Detailed Description Text (22):

The most probable mechanism for photo-oxidation of Kapton involves the excitation of the phthalimide chromophore with ultraviolet light of wavelengths between about 200-300 nm to form a biradical intermediate. It is very likely that this intermediate rapidly reacts with oxygen to form peroxy radicals (ROO.) which also abstract hydrogen atoms to form peroxides (ROOH). The peroxides can easily decompose to alkoxy (RO.) and hydroxy (.OH) radicals which can subsequently react via similar reactions.

Detailed Description Text (24):

It is possible to monitor the progress of the surface activation reaction by measuring the water contact angle of the substrate surface at different times during the activation step. FIGS. 2 to 5 are plots of water contact angle versus time of activation for Kapton, Mylar (PET), PVC and PE, respectively. The water contact angle decreases due to the increased hydrophilicity of the polymer surfaces.

Detailed Description Text (25):

FIG. 2 shows the water contact angle of Kapton as a function of activation time. In a comparison between activation done in air and pure oxygen, no visible dependence on oxygen concentration was observed for activation of Kapton. For short (about 3 to 5 minutes) treatments a relatively high, constant rate reaction is occurring, reducing the water contact angle from 72.degree. to about 10.degree.. For longer treatment times, the surface comes to a steady state with the same contact angle. It

is important to note that the water contact angles were measured immediately after the treatment. For samples stored in air after treatment the contact angles increased to about 50.degree.. It is also important to note that, even though the water contact angle reaches a steady state, the surface composition continues to change throughout the activation step. The inventors have found that shorter treatment times result in high concentrations of reactive hydrogen groups, whereas longer treatment times result in the formation of other oxygen-containing groups, such as (ketone) carbonyl groups.

Detailed Description Text (26):

The following Table I compares compositions of Kapton polyimide, as determined by X-ray Photospectroscopy (XPS), with the theoretical composition.

Detailed Description Text (27):

Table I shows that the ratio of O/C atoms in Kapton increased by a factor of 1.4 following activation. Although not shown in Table I, high resolution XPS indicates that phenolic hydroxyl groups have been formed on the surface of Kapton during the activation.

Detailed Description Text (29):

A comparison of theoretical composition of PEEK with that measured by XPS before and after activation is shown in Table II below. As in the case of Kapton, activation causes an increase in the O/C ratio, the ratio increasing by 2.5 times after activation.

Detailed Description Text (31):

As discussed above, some polymers, for example polyimides, may be activated by a wet process, comprising hydrolysis by a dilute aqueous base, such as NaOH, followed by proton exchange with an acid such as acetic acid. A reaction scheme for wet activation of Kapton is shown in FIG. 6. Hydrolysis and acidification of the polyimide occurs by ring-opening of the imide to form the corresponding carboxylic acid and amide (polyamic acid). 4

Detailed Description Text (32):

Preferably, the base hydrolysis of Kapton is performed in aqueous 0.25 M NaOH at room temperature for about three hours. The polyamic acid salt is preferably then treated with 0.1 M acetic acid for about three hours at room temperature.

Detailed Description Text (44):

Preferably, the silylating agent diffuses into the substrate to react with active hydrogen atoms throughout the activated surface region of the substrate. The diffusion rate of the silylating agent may preferably be increased by slight heating, up to about 60.degree. C., and by the addition, to the silylation bath, of the diffusion enhancer. For polymers such as Kapton, PEEK and PET a diffusion enhancer such as n-methylpyrrolidone (NMP) can be added. It should be noted that the diffusion enhancer is not necessary to the process, it simply acts as an aid to increase the depth and speed of the silylation process.

Detailed Description Text (55):

The silicon and oxygen enriched outer portion of the surface region is a transparent and glass-like. It was found that surface modified Kapton had very similar optical properties as pristine samples, in particular total reflectance (200 to 2450 nm), which covers UV, visible and infrared radiation, was unchanged.

Detailed Description Text (59):

Kapton 500 HN (PMDA-ODA) polyimide sheets with a thickness of 125 .mu.m (5 mil) were obtained from Du Pont.

Detailed Description Text (60):

Aluminized Kapton (Al-Kapton) Polyimide (PMDA-ODA) sheets with a thickness of 76.2 .mu.m (3 mil) aluminized (0.1 .mu.m) on one side, was purchased from Du Pont.

Detailed Description Text (69):

As-received Kapton 5 mil thickness film, measuring 5.times.5 cm was placed 25 mm from UV source in air and was exposed 20 min to a total dose of 3.+-.0.1 J/cm.sup.2

on both sides. After activation the sample had: water contact angle 20.degree., composition of surface by XPS: C-74.5; O-19.0; N-6.5% at. (XPS analyzes the outer most 1 to 2 nm of a surface and provides quantitative measurements of all chemical elements except hydrogen. XPS is also sensitive to bonding type.)

Detailed Description Text (71):

The results from SIMS depth profile analysis indicates that the penetration of Si into the Kapton exceeds 0.5 .mu.m. Based upon both Si and 180 distributions in the subsurface layer it is obvious that an oxide-based layer, with a thickness of 1000 to 1500 .ANG. and a graded distribution of these elements, is formed in the material.

Detailed Description Text (73):

Example 1 was repeated, except that the Kapton film was cleaned ultrasonically for 10 min in a solution of ethanol and dried in an oven at 100.degree. C. for 60 min. After oxidative stabilization the sample had: water contact angle 0.degree., composition of surface C-18; O-48; N-3; Si-31% at.

Detailed Description Text (77):

As received aluminized Kapton, measuring 5.times.5 cm, was placed 25 mm from UV source in air and exposed for 20 min to a total dose of 3.+-.0.1 J/cm.sup.2. After activation the sample had water contact angle 20.degree.. The film was then silylated in a solution of 31% B[DMA]DS in p-xylene containing 7% NMP for about 10 min at 55.degree. C. in a beaker heated on a hot plate. The film was then washed in p-xylene, blown dry with air at room temperature. After silylation the sample had a water contact angle of 92.degree.. Next, the film was placed 25 mm from the UV source in air atmosphere and was exposed to a total dose of 14.0.+-.0.5 J/cm.sup.2. After oxidative stabilization the sample had: water contact angle 0.degree., composition of surface C-24; O-52; N-1.6; Si-22% at.

Detailed Description Text (79):

Example 4 was repeated except that, before activation, the Al-Kapton film was cleaned ultrasonically for 10 min in a solution of ethanol and oven dried at 100.degree. C. for 60 minutes. After oxidative stabilization the sample had; water contact angle 0.degree., surface composition C-26; O-54; N-0; Si-20% at.

Detailed Description Text (114):

Additional surface modification experiments were conducted with samples of PEEK and Kapton, and Tables VIII and IX below show the water contact angles and the surface compositions, as determined by XPS, for these samples.

Detailed Description Text (115):

FAO testing was conducted on a number of Kapton samples and the results are summarized in Table X, which shows the surface modification conditions under which the samples were prepared and the surface composition, as determined by XPS, of the samples.

Detailed Description Text (118):

Thermal cycling of silylated Kapton samples was conducted to estimate the mechanical and thermal properties of the modified materials. Liquid nitrogen dipping and fast transfer to the preheated oven at 120.degree. C. and atmospheric pressure were used in six cycles with a period of about 20 minutes and amplitude of +120 to -180.degree. C.

Detailed Description Text (119):

SEM analysis of samples before and after thermal cycling indicated slight morphological differences between the modified, silylated Kapton surface and the same surface after six thermal cycles. No cracking, however, was found on the surface of the thermally cycled sample, leading to a conclusion that the modified layer had a good thermal stress match with the bulk material.

Detailed Description Text (122):

In the following experiments, corona discharge was used for activation and/or oxidative stabilization of Kapton and polyethylene films. In Example 17, corona discharge was used both for activation and oxidative stabilization, whereas in

Examples 18 and 19, corona discharge was used only for activation and oxidative stabilization, respectively. As shown by the results of Examples 17 to 19, corona discharge is acceptable both for activation and oxidative stabilization.

Detailed Description Text (127):

As-received 2 mil thick Kapton polyimide film measuring 10.times.10 cm was activated by corona discharge at an energy of 40 mJ/mm.sup.2. After activation, the sample exhibited a water contact angle 24.degree..

Detailed Description Text (130):

Example 17 was repeated, except that the Kapton polyimide film after activation and silylation was oxidatively converted by exposure to UV in air at a distance of 25 mm from the UV source and exposed to a total dose of 2 J/cm.sup.2. After oxidative stabilization the sample had a water contact angle of 0.degree. and a surface composition of C-52.0, O-35.2, N-5.6, Si-7.2% at.

Detailed Description Text (132):

Example 17 was repeated, except that the Kapton polyimide film was activated by UV in air. The sample was placed 25 mm from the UV source and was exposed for 10 minutes to a total dose of 1.3 J/cm.sup.2 on both sides. After activation the sample had a water contact angle of 36.degree., after silylation--87.degree., and after oxidative stabilization the sample had a water contact angle of 0.degree. and a surface composition of C-53.4, O-32.8, N-5.6, Si-8.2% at.

Detailed Description Text (134):

Example 17 was repeated with Polyethylene 2.8 mil thick film instead of Kapton polyimide. The silylation was done in a solution of 25% B[DMA]DS in p-xylene for about 10 minutes at 40.degree. C. After oxidative stabilization the sample had a water contact angle of 74.degree. and a surface composition of C-44.5, O-36.1, N-1.1, Si-18.3% at.

Detailed Description Text (136):

The following Example 21 describes a preferred process for wet activation of Kapton polyimide.

Detailed Description Text (138):

As received 5 mil thick Kapton polyimide film measuring 10.times.10 cm was activated in a wet process as disclosed in M. M. Pleahaty and R. R. Thomas, J. Electrochem. Soc., 139(3), 810 (1992) by hydrolysis in an aqueous 0.25M NaOH-solution for 3 hours at room temperature. At this stage, a portion of the polyimide has been converted to the sodium salt of polyamic acid. The salt was converted to the amic acid form after treatment with an aqueous 0.1 M acetic acid solution for an equal period of time and temperature. After activation, the sample had a water contact angle of 51.degree. and a surface composition of C-77, O-15, N-6.2% at.

Detailed Description Text (173):

The process of the present invention may also be used to produce membranes having unique properties. As discussed above, the present invention permits surface treatment of one side of a film or membrane, and therefore membranes may be provided having different wettabilities on their two sides. This may affect fluid transfer and increase through rate of membranes such as reverse osmosis membranes.

Detailed Description Text (174):

Other membranes which may be treated according to the present invention are bio-compatible medical membranes and "artificial skin", with the surface modification process of the present invention being used to improve bio-stability and blood and tissue compatibility of such membranes.

Detailed Description Text (177):

The process of the present invention may also be used to improve adhesion between other problematic combinations of materials. For example, it may be desirable to provide polymer coatings treated according to the present invention on steel to improve adhesion of paints thereto, and for example to enhance adhesion of urethane and siloxane in medical devices. Similarly, electronic devices frequently contain metallized polymers such as copper-coated Kapton. Treatment of Kapton according to

the present invention prior to metallization may help adhesion to the metal film.

Detailed Description Paragraph Table (1):

TABLE I Sample composition of Kapton  
Polyimide as determined by XPS Sample and Composition, at % Treatment Carbon Oxygen  
Nitrogen O/C Theoretical Polyimide 75.9 17.2  
6.9 0.23 Control: Surface 79.6 14.3 5.4 0.18 "Bulk" 14.4 5.8 0.18 Exposure UV in air  
75.0 19.0 6.5 0.25 Wet Process 15.07.0 6.2 0.19

Detailed Description Paragraph Table (3):

TABLE III A Summary of Water Contact Angle  
Values for Materials as Measured After Different Stages of the Modified Silylation  
Process, 20.degree. C. Water Contact Angle After Different Stages in the Process  
[deg] Pristine Oxidatively Polymer (untreated) Activated Silylated Converted  
Kapton 500 HN Example 1 72 21 90 4 Example 2  
20 91 0 Example 3 22 89 0 Al-Kapton Example 4 85 21 92 0 Example 5 85 20 93 0  
Example 6 85 22 93 0 PEEK Example 7 72 22 133 0 Mylar Example 8 77 37 101 0 Example  
9 77 25 101 9 Example 10 77 22 106 18 Polyethylene Example 11 102 33 99 72 PVC  
Example 12 82 60 105 19 Example 13 82 23 105 0 AS4 Fiber APC-2 PEEK Resin 72 12 79  
22 3501-6 Epoxy Resin 79 18 85 12 AS4 Fibers .about.90 <30 .about.90 <30

Detailed Description Paragraph Table (4):

TABLE IV Summary of X-ray Photospectroscopy  
(XPS) Analyses Based on Results Described in Examples 1-16 After final stage of  
formation, (at. %) Sample C O Si N Kapton  
(example 1) 17 49 34 Aluminized Kapton (example 4) 24 52 22 1.6 PEEK (example 7) 26  
48 26 Mylar (example 8) 28.4 47.5 23.6 Polyethylene (example 11) 41.1 39.3 19.6 PVC  
(example 13) 30.8 47 21.1 Carbon fibre/PEEK (example 14) 20.8 52.7 25.6 0.7 Carbon  
fibre/Epoxy (example 15) 18 55.1 25.4 1.4 PAN based carbon fiber (example 16) 46.9  
27.5 25.6

Detailed Description Paragraph Table (5):

TABLE V High Resolution XPS Data Peaks Be, eV  
Atomic % Kapton C 1s 284.7 91.0 286.0 9.0 Si  
2p 101.9 35.3 103.3 43.2 104.0 21.6 O 1s 531.6 14.6 532.8 85.4 Al-Kapton C 1s 284.7  
14.1 286.1 51.9 287.6 18.6 289.7 10.4 291.5 5.0 Si 2p 103.2 38.4 104.7 41.1 105.3  
20.5 O 1s 532.7 36.8 534.2 63.2 PEEK composite C 1s 283.2 3.5 284.7 59.1 286.1 20.8  
287.2 7.8 288.5 5.6 289.5 3.1 Si 2p 102.6 27.9 103.6 61.0 104.7 11.1 O 1s 531.2 3.0  
533.0 93.4 534.8 3.7 Epoxy composite C 1s 283.5 4.3 284.8 69.0 285.9 13.1 287.4 6.4  
289.6 1.8 292.2 5.1 Si 2p 102.4 22.2 103.6 64.5 104.7 13.3 O 1s 532.1 14.3 533.1  
66.5 534.0 19.2

Detailed Description Paragraph Table (6):

TABLE VI XPS Surface Composition (atomic %)  
of Polymer Samples After Different Stages of Treatment Elements Detected Sample C O  
N Si Other Kapton Pristine 79.6 14.3 5.4 --  
-- After silylation 65 16 5.2 14 -- After oxidative stabilization 17 50 -- 34 --  
Al-Kapton Pristine 67.8 23.1 2.1 1.8 5.3 Al After silylation 57 20 -- 23 -- After  
oxidative stabilization 38 39 -- 23 -- Mylar Pristine 78 22 -- -- 0.8 Sn After  
silylation 58 21 -- 20 0.6 Sn After oxidative stabilization 36.6 43.4 -- 20.3 --  
Polyethylene Pristine 97 2.6 -- -- 0.7 Sn After silylation 68 16 -- 16 -- After  
oxidative stabilization 41.1 39.3 -- 19.6 -- PVC After silylation 51.2 24.8 -- 22.8  
0.6 Cl After oxidative stabilization 30.8 47.0 -- 21.1 --

Detailed Description Paragraph Table (7):

TABLE VII Erosion Yield for Materials  
Material Erosion Yield (g/atom) Kapton 500 HN  
Pristine 4.3 .times. 10.sup.-24 After functionalization <5.5 .times. 10.sup.-26  
Al-Kapton Pristine 4.3 .times. 10.sup.-24 After functionalization <5.5 .times.  
10.sup.-26 PEEK Pristine 2.8 .times. 10.sup.-24 After functionalization <7.9 .times.  
10.sup.-26 Polyethylene Pristine 3.6 .times. 10.sup.-24 After functionalization <5.9  
.times. 10.sup.-26 Carbon Fiber/PEEK Pristine 2.2 .times. 10.sup.-24 After

TABLE X						XPS Surface Composition (at. %) of Kapton after FAO Testing Elements Detected Sample Treatment Controls C O Si N Si/C								
						Control --		70 24 --		5.7 --		56-3 Silylated		47
41	8.7	3.0	0.18	56-1	Photo-oxidized 20 min., Silylated,	16	63	21	0.1	1.3	Annealed			
56-2					Photo-oxidized 20 min., Silylated,	17	54	28	1.5	1.6	Annealed, Oxidatively			
					Converted 60 min.	37					Wet process activation, Silylated,	17	57	26
					Oxidatively Converted 60 min.	36					Wet process activation, Silylated,	14	53	33
					Oxidatively Converted 60 min.							0.6	2.3	